



# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Decationized Molecular Sieve Compositions

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organized under the laws of the State of New York, United States of America, (Assignee of JULE ANTOINE RABO, PAUL EUGENE PICKERT and JAMES EDWARD BOYLE) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to decationized crystalline zeolitic aluminosilicates of the molecular sieve type and to methods for their preparation.

Zeolitic molecular sieves are natural or synthetic crystalline metal aluminosilicates having a highly ordered arrangement of  $AlO_4$  and  $SiO_4$  tetrahedra which are interconnected through shared oxygen atoms. The spaces between the tetrahedra are occupied by water molecules prior to dehydration. Dehydration results in crystals interlaced with channels of molecular dimensions. These offer very large surface areas for the absorption of foreign molecules provided the crystal structure remains intact so that the openings into the internal adsorption areas are retained.

The electrovalence of the aluminum in the structure is balanced by the inclusion of a cation in the crystal. In synthetic zeolitic molecular sieves the cation is most commonly an alkali metal such as sodium and potassium or mixtures thereof. The cations of either the synthetic or naturally occurring zeolites can be exchanged for other mono-, di- or trivalent cations which are of a suitable physical size and configuration to diffuse into the intracrystalline passages in the aluminosilicate structure.

The substitution of the original cations of the aluminosilicate with hydrogen cations by acid or water leaching has been heretofore known in the art. In addition, the intro-

duction of hydrogen cations as substitutes for the metal cations has also been accomplished heretofore by ion-exchanging the metallic cations with ammonium cations and thereafter thermally treating the ammonium-exchanged form to liberate ammonia gas.

In these instances, however, the original metallic cation was either replaced by another metallic cation or by a hydrogen cation. Heretofore, it was thought that the aluminosilicate framework of the crystalline zeolitic molecular sieves was inherently unstable, i.e., its crystalline structure would be destroyed, unless the aluminum atoms in that framework were stabilized by the presence of a stable cation and heretofore all efforts to produce large pore decationized molecular sieves having their essential crystalline structure unimpaired have met with failure.

This invention comprises a decationized aluminosilicate zeolitic molecular sieve having a crystalline structure, a silicon dioxide to aluminum trioxide molar ratio greater than 3.0a, pore size of at least 5.6Å, capable of adsorbing benzene, and in which at least 10% of the aluminum atoms of the zeolitic molecular sieve are not associated with cations.

The silicon dioxide to aluminium trioxide molar ratio is preferably greater than 4.5 and it is preferred that at least 30%, more preferably at least 70%, of the aluminium atoms of the zeolitic molecular sieve are not associated with cations.

This invention also comprises a process for the preparation of a decationized zeolitic aluminosilicate molecular sieve which comprises contacting a crystalline zeolitic molecular sieve having a silicon dioxide to aluminum trioxide ratio of greater than 3.0 and a pore size of at least 5.6Å, with a hydrogen or ammonium cation containing material thereby replacing at least 10% of the zeolitic cations with hydrogen or ammonium cations by heating the substituted zeolite at a temperature of from 350° C. to 600° C.

[Prior]

Prior

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The process by which the novel materials of this invention are produced may be called "decationization". The decationized molecular sieve aluminosilicates produced thereby have at least some of their aluminum atoms unbalanced by cationic substituents and yet have unimpaired crystalline configuration. Therefore, in addition to the adsorbent properties of all molecular sieves, these decationized materials are useful as hydrocarbon conversion catalysts. Among the hydrocarbon converting processes which may be catalyzed by the novel compositions of this invention are cracking or hydrocracking processes. In addition the novel compositions of this invention will act as "supports" for the same as disclosed in our British Patent application No. 43205/60 [Serial No. 972,832], the description thereof being incorporated herein by reference.

It should be noted that, in order to effect structural rearrangement of hydrocarbon molecules it is essential that the novel decationized sieves of this invention possess pore sizes sufficient to adsorb the hydrocarbon molecules and desorb the rearranged hydrocarbon molecules. Examples of the zeolites that may be employed in the practice of this invention are large pore size naturally occurring zeolites such as fawcites and large pore size synthetic zeolites which shall be hereinafter referred to as "Y" and "L".

Zeolite Y, its preparation and identification are described in British Patent Specification No. 909,266 and British Patent Application No. 43203/60 [Serial No. 972,831].

Zeolite L, its preparation and identification are described in British Patent Specification No. 909,264.

For the purposes of our invention, the removal of the zeolitic cations and the replacement thereof by hydrogen cations via the method of water leaching is not preferred since the removal of more than 30 per cent of the zeolitic cations by this method is not possible. It is within the scope of this invention, however, to employ leaching with water to remove some of the zeolitic cations followed thereafter by additional decationization by other methods.

For the purposes of our invention, the replacement of the metallic cations of the zeolitic molecular sieve with hydrogen ions by ion exchange with aqueous acids, prior to decationization by thermal treatment, is also not a preferred method. This is because the molecular sieve zeolites are less stable in strongly acid mediums than in neutral or basic media.

In this regard, it should be noted that aqueous slurries of the alkali metal cation forms of molecular sieves are generally basic having a pH between 10 and 12. Following the above indicated procedure, when these slurries are treated with acids to obtain hydro-

gen cation-exchange the method may be compared to the titration of a base with an acid. As the titration proceeds, however, a buffered region results in the titration curve where the consumption of the hydrogen cation of the acid through ion-exchange with the zeolite cation is not complete. As a consequence thereof, the excess acid attacks the zeolite framework with the dissolution of the alumina and a subsequent loss in zeolite crystallinity. In the buffered region of the titration curve the addition of acid does not appreciably change the pH of the slurry. With the type "X" zeolite of British Patent Specification No. 777,233 the buffering occurs at a pH of 3.5-4 and with the type Y zeolite at a pH of 2.5-3.0. Therefore, these pH values set a limit to the type and amount of mineral acid that can be used for this type of ion-exchange.

Generally, any easily ionizable acid can be used providing the quantity used does not lower the pH to these values. Acids that have been used for this purpose include hydrochloric (representative of the strong mineral acids) and acetic acid (representative of the weak acids).

Ammonium-ion exchange of the molecular sieve to obtain the novel compositions of this invention is preferred. Such exchange can be effected by a batch process wherein the molecular sieve is slurried in an aqueous ammonium salt solution and the ion exchange equilibrium established. Alternatively the exchange can be effected by a continuous technique wherein a solution of ammonium cation is passed over a column of the zeolite and the effluent containing the formed salt is continuously removed.

The second method is favoured for high percentages of ion exchange. For example, in a 85-100 per cent removal of the zeolite cation by ion exchange, a heated, continuous exchange technique is desirable. It is usually necessary to have repeated batchwise ion-exchanges in order to remove the additional zeolite cations. However, the efficiency of the exchange decreases as the number of batchwise exchanges increases and approaches a limit at about 90 per cent exchange. Batchwise ion exchanges at elevated temperatures of 80 to 100° C. are more efficient than similar exchanges at room temperature for ion exchanges over 50 per cent.

Any soluble ammonium salt can be used to effect the ion exchange of the zeolitic cation providing the resulting salt formed during the ion exchange is soluble. If the formed salt is insoluble it may be precipitated within the pores of the zeolite and would be very difficult to remove by washing. Since most common ammonium salts are water soluble, this limitation is concerned primarily with the zeolitic cation to be exchanged, i.e., a silver-exchanged zeolite exchanged with

ammonium chloride solution would result in the formation of insoluble AgCl. In this case a solution of ammonium nitrate would be preferred since AgNO<sub>3</sub> is soluble in H<sub>2</sub>O, the preferred exchanging medium. It is to be understood, moreover, that quaternary ammonium cations, as exemplified by tetramethylammonium ions, can also be employed in the practice of our invention.

Since molecular sieve zeolites are usually synthesized in the alkali metal cation form, most of the ammonium ion exchanges will be effected with these alkali metal cations. However, ammonium ion exchange with the other cation-containing zeolites is possible within the previously mentioned limits. For example, a 90 per cent calcium ion-exchanged type Y zeolite may be ammonium ion-exchanged.

It may be desirable at times to acid wash, within the above mentioned limitations of this process, zeolites prior to the ammonium ion exchange to effect a certain degree of hydrogen cation exchange. This may also be done to effect the removal of difficultly removable impurities in the zeolite such as sodium silicate, sodium aluminate or sodium hydroxide remaining from the synthesis of the zeolite. Hence, this procedure serves as a purification process prior to effecting ion exchange to a high degree.

It is well known that the crystallinity of zeolitic molecular sieves may be demonstrated by characteristic X-ray diffraction patterns and adsorption characteristics. These characteristics include the type of adsorption, as

shown by the shape of the adsorption isotherm, and uniformity of pore size. The latter is measurable through selectivity measurements with molecules having known cross sections.

Similarly, the novel crystalline decationized zeolitic aluminosilicates of this invention may also be identified by their molecular sieve adsorptive properties and the pore size of the decationized zeolitic molecular sieves of this invention must be sufficient to permit adsorption of benzene. Moreover, the sieves are also recognizable by their aluminosilicate framework wherein silica and alumina are in a ratio greater than 3.0. Finally, they may also be identified since they retain the characteristic X-ray diffraction pattern of the particular cationic zeolitic molecular sieve employed for the decationization process.

Cation exchange of the sodium ions of the molecular sieve zeolites will usually result in a slight change in the peak-heights (intensity) of the X-ray diffraction pattern relative to the original sodium form. However, no new peaks will be formed and all of the major peaks will be retained, thereby indicating no change in the basic crystalline structure of the zeolite. For example synthetic sodium zeolite "Y", Na(100)Y, was thoroughly cation exchanged to silver zeolite Y, Ag(100)Y, which was then thoroughly cation exchanged to ammonium zeolite Y, NH<sub>4</sub>(100)Y. Samples from each were submitted for X-ray identification. The results are tabulated below:

Zeolite Form	Sum of 10 Similarly Spaced Major Peak-Heights	Sum of 10 Similarly Spaced Minor Peak-Heights
Na(100)Y	348	75
Ag(100)Y	125	33
NH <sub>4</sub> (100)Y	369	70

The terms "decationized" or "decationization" are selected to characterize the novel zeolitic catalysts of this invention and the process for their preparation. As indicated heretofore, the decationization of the ammonium or hydrogen cation exchanged molecular sieve zeolites of this invention is generally accomplished by thermally heating the zeolite to temperatures between 350° C. and 600° C.

While the exact mechanism of the decationization process is not fully understood, the following equations showing the decationization of an ammonium cation exchanged zeolitic molecular sieve can be taken as illustrative:



It is noted that water is evolved in the second equation of the decationization process. This water is believed to be formed from hydrogen from the cation sites and an equivalent amount of oxygen released from the aluminosilicate framework. That the crystal framework does not collapse when these oxygen atoms are removed is surprising. It is believed that this stability is attributable to the silica to alumina ratio of greater than 3. This is substantiated by the fact that such a ratio has been found to be essential in the formation of the novel compositions of this invention.

It has also been found that, upon rehydration, cations can be reintroduced to a substantial extent. This indicates the presence of cation receptive sites in the decationized

structure. These cation receptive sites are the result of the unpaired electrons remaining in the aluminum oxide tetrahedra as a result of the decationization steps.

5 The removal of the ammonia is facilitated by carrying out the heating in an oxygen-containing atmosphere, such as air, while a vacuum helps in removing the water. The temperature employed in the removal of  
10 ammonia is critical, i.e., it must be in the range of 350° C. to 600° C., and preferably in the range of 475° C. to 600° C. When the decationized zeolitic molecular sieve is to be employed in hydrocarbon conversion  
15 processes, it is permissible to carry out the thermal treatment *in situ* after the metal cations of the zeolitic molecular sieve have been exchanged for the removable ammonium or hydrogen cations.

20 Therefore, it is to be clearly understood from the foregoing, that the term "decationized" relates to that unique condition whereby a substantial amount, i.e., at least 10 per cent of the aluminum atoms of  
25 the aluminosilicate structure are not associated with cations. Another way of expressing "decationization" is that condition whereby less than 90 per cent of the aluminum atoms of a metal aluminosilicate zeolitic molecular

sieve are associated with cations.

For best catalytic results, the degree of decationization should be at least 30 per cent and preferably higher. It is to be observed that at about the preferred degrees of decationization of our catalyst, a zeolite "X" molecular sieve, as disclosed in British Patent Specification No. 777,233, loses its crystallinity. By contrast, a decationized zeolite "Y" of our invention will retain its crystallinity even when 100 per cent decationized.

To indicate this, a series of large pore-size zeolites which had been ammonium cation exchanged in varying amounts, were heated. After exposure to atmospheric air, they were subjected to X-ray examination. The exposure to moist air allowed uncontrolled rehydration to occur. The intensities of the X-ray lines were, in general, diminished only slightly except in the sample employing zeolite X which has a silica to alumina ratio of 2.5. The results of these tests are presented below wherein the degree of ammonium cation-exchange is shown in parenthesis in the zeolite formulas. The results are shown as a percentage of the sum total retention of the peak heights of the 10 major lines.

Effect of Thermal Decomposition Conditions on the Retention of X-ray Diffraction Pattern Peak-Heights of Decationized Zeolite

Firing Conditions	% Retention of Peak-Heights				
	NH <sub>4</sub> (80)X	NH <sub>4</sub> (20)Y	NH <sub>4</sub> (40)Y	NH <sub>4</sub> (60)Y	NH <sub>4</sub> (80)Y
None	100	100	100	100	100
In air to 350° C.	—	90	80	70	55
In vacuum to 350° C.	—	90	80	70	55
In air to 350° C., rehydrated and heated again in air to 350° C.	—	90	75	35	—
In air to 600° C.	—	80	80	60	30
In vacuum to 600° C.	10	100	85	80	60

60 As indicated previously, the materials of this invention can also be rehydrated and reactivated without loss of the essential molecular sieving characteristics of the material. Repeated adsorption-desorption of hydrocarbon and other non-polar molecules on  
65 decationized materials does not alter the adsorption characteristics of the materials. This is because the crystallinity of the decationized molecules is not destroyed. If all or even a portion of the zeolitic crystallinity were destroyed, a certain amount of

the pores, relative to the degree of destruction, would be opened or closed with a subsequent reduction in the molecular sieving effect. The adsorption of the critical size molecule on the amorphous portion formed during destruction would, therefore, result in a subsequent increase in the adsorption capacity and the destruction of the selective adsorption characteristics of the materials.

The results of such adsorptions on decationized Types X and Y Molecular Sieve zeolites are presented below.

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ADSORPTION OF CRITICAL SIZE MOLECULES ON  
DECATIONIZED MOLECULAR SIEVE ZEOLITES AT 25° C.

Pressure	20 mm. Hg	0.075 mm. Hg	0.075 mm. Hg
Adsorbate	Perfluoro C <sub>8</sub> Cyclic Ether	Tri-n-Butylamine	Perfluoro-Tri- n-Butylamine
Material	Adsorption Capacities (a)		
	Critical Dimension $\approx$ 7.5 Å	Critical Dimension $\approx$ 9.1 Å	Critical Dimension $\approx$ 11.5 Å
NaY Standard (b)	41.7	19.1	3.9
NH <sub>4</sub> (20)Na(80)Y(b)	42.4	18.5	4.3
NH <sub>4</sub> (65)Na(35)Y(b)	42.3	4.2	1.2
NH <sub>4</sub> (80)Na(20)Y(b)	39.7	3.3	2.9
NH <sub>4</sub> (80)Na(20)Y — original activation at 500° C., rehydrated and reactivated at 350° C.	26.3	3.6	2.2
NH <sub>4</sub> (80)Na(20)Y — original activation at 350° C., rehydrated and reactivated at 350° C.	25.2	3.2	2.1
NH <sub>4</sub> (80)Na(20)X — original activation at 500° C., rehydrated and reactivated at 350° C.	17.0	6.3	12.7
NH <sub>4</sub> (80)Na(20)X — original activation at 350° C., rehydrated and reactivated at 350° C.	25.4	10.0	20.9

(a) g. adsorbate/g. activated absorbent  $\times 100$

(b) activated at 350° C. in vacuum

The extent of decationisation of the materials used in the above table is indicated by the number in parentheses after NH<sub>4</sub>. Thus NH<sub>4</sub>(65)Na(35)Y yields a 65% decationised zeolite Y with 35% of the original cations remaining.

5 All the materials tested regardless of the  
degree of ammonium exchange or decationiza-  
tion adsorbed a substantial quantity of the  
perfluoro C<sub>8</sub> cyclic ether. Adsorption of tri-  
n-butylamine on these same materials indi-  
cated that products from ammonium ion ex-  
changes greater than 20 per cent had an  
apparent decrease in pore size. None of the  
10 products according to the invention adsorbed  
the large perfluorinated tri-n-butylamine  
illustrating the unique uniform pore size of  
these materials after such an activation.

By comparison with the 80 per cent ammo-  
nium cation-exchanged Type X zeolite, heat-  
ing at either 350° C. or 500° C. followed  
by saturation with water and reheating  
showed a decrease in the molecular sieving  
effect (amorphous material formation) in that  
both the tri-n-butylamine and the perfluoro-  
tri-n-butylamine were adsorbed. Similarly,  
the adsorption capacities of these two  
materials for the perfluoro C<sub>8</sub> cyclic ether  
was reduced to approximately 50 per cent  
of the value of the materials before rehydra-  
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tion. A similar decrease in adsorption capacity for normal hexane, a smaller molecule, was also found.

- 5 With a similarly decationized Type Y Molecular Sieve zeolite, treated in the same manner as that described for the Type X zeolite, a loss in the adsorption capacity for the perfluoro  $C_8$  cyclic ether equivalent to the decrease in the n-hexane adsorption capacity was observed. However, regardless of the decationization temperature, this material did not adsorb the larger size adsorbates. These results demonstrate that the decationized materials still have a uni-
- 10 form pore size characteristic of a crystalline molecular sieve zeolite.
- 15 The following examples will serve to illustrate the practice of this invention:

#### EXAMPLE I

- 20 (a) Two hundred grams of a NaY molecular sieve zeolite having a  $SiO_2:Al_2O_3$  ratio of 4.8 and containing 18 wt-%  $H_2O$  was suspended with mechanical stirring in 400 ml. of distilled water. To this slurry portions of a 2.35 N aqueous hydrochloric acid solution
- 25 were added. The pH was measured after each addition. The following values were obtained:

	Ml. of Acid Added	pH of Slurry
30	0	9.90
	25	4.70
	50	3.60
	75	3.30
	100	3.00
35	125	2.80
	150	2.70
	175	2.60
	200	2.55

This corresponded to the addition of 0.470 equivalents of acid which is enough for 65% removal of the sodium if the exchange were quantitative. The exchanged zeolite was filtered with suction and washed with distilled water until the washings gave a negative test for  $Cl^-$  with silver nitrate reagent. The analysis of this material showed a 48% removal of the original sodium content. All zeolite crystallinity was retained as evidenced by X-ray patterns.

(b) To the same quantity of NaY zeolite used in Example I (a) there was added 100 ml. of 2.35 N HCl. The slurry pH was 3.1. This was enough acid theoretically for a 33% exchange of the sodium cation. Analyses showed a 30% ion exchange of the sodium had been achieved. All crystallinity was retained.

#### EXAMPLE II

##### Ammonium Exchange of Type Y Molecular Sieve Zeolite (Batchwise)

A series of various  $NH_4^+$  exchanged type Y zeolites were prepared to determine the effect of the ratio of  $NH_4^+/Na^+$  equivalents. For each sample 290 grams of type Y molecular sieve was used. The sieve contained 20%  $H_2O$ . The necessary amount of  $NH_4Cl$  was dissolved in enough distilled  $H_2O$  (taking into consideration the 60 ml. of  $H_2O$  present on the zeolite) to produce a 1.0 molar solution for each determination. The zeolite was added to the solutions, the resulting slurry was stirred for 0.5–20 hours and then filtered with suction. The solids were washed free of chloride ion with fresh distilled water. The following data were found:

Preparation			Analyses		
$NH_4^+/Na^+$ Equivalents Ratio	Grams $NH_4Cl$	$H_2O$ Content Minus 60 Ml.	% $(NH_4)_2O$ Anhydrous Basis	% $Na_2O$ Anhydrous Basis	% Na Not Removed
0.35	19	290	3.1	9.1	68
0.50	27	440	4.0	8.0	60
1.0	54	940	5.7	6.1	45
2.0	108	1940	6.9	4.7	35
4.0	216	3940	7.5	4.1	31

#### EXAMPLE III

##### Batchwise Ammonium Exchange Type Y Molecular Sieve

- 80 Thirteen hundred twenty (1320) grams of a NaY molecular sieve zeolite having a  $SiO_2:Al_2O_3$  ratio of 4.7 were suspended in 2 liters of distilled  $H_2O$ . To this suspension

was added a solution of 2140 g. (40 equivalents) of  $NH_4Cl$  dissolved in 6 liters of distilled water that had been heated to boiling. The resulting suspension was stirred for 2 hours without additional heating and was then cooled to room temperature. The suspension was filtered with suction and the filtered pro-

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duct washed with 3 liters of distilled  $H_2O$ . This process was repeated five times. The 5 times-exchanged material was washed free of chloride ion as were the small samples removed after each exchange, dried in an

oven at  $125^\circ C$ . and then re-equilibrated with the  $H_2O$  vapor in air. The following analyses were obtained after the third, fourth and fifth exchanges:

Na <sub>2</sub> O Anhydrous Basis			(NH <sub>4</sub> ) <sub>2</sub> O—(Anhydrous Basis)	
No. of Exchanges	Wt—% Found	% of Original	Wt—% Found	% of Exchange
3	2.3	19	9.0	82
4	2.0	16	10.0	84
5	1.8	14	10.1	86

#### EXAMPLE IV

##### Continuous Ammonium Exchange of Type Y Molecular Sieve Zeolite

Two hundred eighty (280) grams of a type NaY molecular sieve zeolite was slurried in 1 liter of distilled water and filtered under a water aspirator vacuum of 20 mm. of Hg. A solution of 216 g. (4.0 moles) of ammonium chloride dissolved in 2 liters of distilled water was drawn through the solids. The cation-exchanged solids were washed free of  $Cl^-$  ion and dried to a free-flowing powder containing 32%  $H_2O$ . Analysis showed the material contained 2.5%  $Na^+$  and 4.1%  $NH_4^+$ .

#### EXAMPLE V

##### Cation Reconstitution of Decationized Sieve

(a) A sample of an ammonium exchanged type Y molecular sieve zeolite was prepared by the continuous ion exchange technique. Analysis showed this material to contain 3.1%

$Na_2O$  and 8.7%  $(NH_4)_2O$  (78% ion-exchanged). This sample was then heated in a stream of dry air to  $510^\circ C$ . for 6 hours, then rehydrated by exposing to air for 20 hours. Analysis of this material showed the following:

$Na_2O = 2.9 \pm 0.1\%$ ;  $H_2O = 19.6 \pm 0.5\%$ ;  $(NH_4)_2O = \text{less than } 0.2\%$ .

(b) The product obtained in (a) above was re-ion exchanged by the passage of 0.432 equivalents of each of the salt solutions indicated below dissolved in 400 ml. of distilled  $H_2O$ , over 31.2 gram samples of zeolite supported on a filter as described in Example IV. The re-ion exchanged samples were washed with distilled  $H_2O$  to remove soluble salts. The samples were thereupon dried in air ( $125^\circ C$ ). Re-ion exchanges were attempted with the following materials with the indicated results.

TABLE M

Re-Ion Exchanging Salt Solution	Analytical Results (Anhydrous Basis)
$NH_4Cl$	$(NH_4)_2O$ , 6.45%; $Na_2O$ , 1.45%
$NaCl$	$Na_2O$ , 7.5%
$NaOH$	$Na_2O$ , 9.6%
$AgNO_3$	$(Ag_2O)$ , 27.3%; $Na_2O = 0.1\%$

Complete cation reconstitution was not achieved in these samples. However, it can be seen that a considerable portion of the cation capacity occupied by  $NH_4^+$  ions before decomposition was still present. In the  $NH_4Cl$  and  $AgNO_3$  re-ion exchanges, additional  $Na^+$  was removed. All of these products had X-ray diffraction patterns characteristic of zeolite Y.

#### EXAMPLE VI

##### Preparation of A Completely $NH_4^+$ Exchanged Molecular Sieve Zeolite

With a Y zeolite, a 100% exchange of the  $Na^+$  ions was accomplished with an  $Ag^+$  ion. The  $Ag$  (100%) Y zeolite was then cation exchanged with solutions of ammonium salts having anions that form an only slightly dissociated anionic complex with the  $Ag^+$

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cation i.e., with a  $\text{CN}^-$  ion which with  $\text{Ag}^+$  forms  $\text{Ag}(\text{CN})_2^-$ , and with a  $\text{SCN}^-$  ion, with which  $\text{Ag}(\text{SCN})_2^-$  forms. Since the silver is in the anionic portion of such a complex it cannot be ion exchanged at the decationized alumina tetrahedra sites of the zeolites. The cationic portion of the complexing salt occupied the sites vacated by the  $\text{Ag}^+$  cations.

#### EXAMPLE VII

##### 10 $\text{NH}_4$ Ion Exchange of A Ca(87) Na (13) Type Y Molecular Sieve Zeolite

A total of 330 g. (247 g. anhydrous) of calcium exchanged Type Y molecular sieve zeolite containing 1.7 wt-%  $\text{Na}_2\text{O}$  and 11.3 wt-%  $\text{CaO}$  was slurried in 1 liter of a solution of 550 g. (10 moles) of  $\text{NH}_4\text{Cl}$  dissolved in 3 liters of distilled  $\text{H}_2\text{O}$ . This slurry was filtered with suction. The remaining 2 liters of the  $\text{NH}_4\text{Cl}$  solution was then passed through the solids. The solids were washed free of the soluble salts, dried in an oven at  $130^\circ\text{C}$ . and left to re-equilibrate with the water vapor in the air (Concentration of moisture in the air 21%). Analyses of the material showed it contained 2.75 wt-%

$\text{CaO}$  (24.4% of that of the starting material), 1.3%  $\text{Na}_2\text{O}$  (9% of that of the starting material) and 8.7 wt-%  $(\text{NH}_4)_2\text{O}$  [74% of a complete  $\text{NH}_4(100)\text{Y}$ ].

#### EXAMPLE VIII

##### Decomposition Under Vacuum

Weighed samples (20—30 g.) of Type Y molecular sieve zeolites ammonium-exchanged to various degrees were placed in Pyrex ("Pyrex" is a registered Trade Mark) glass tubes sealed at one end, and heated under a vacuum of 0.1—0.5 mm. of Hg. The amount of  $\text{NH}_3$  gas liberated was collected in a trap containing water to which known amounts of standardized sulfuric acid solution could be added semicontinuously as the  $\text{NH}_3$  was collected. Bromocresol purple was the visual acid-base indicator in this trap. The amount of  $\text{NH}_3$  liberated as the sample was heated to different temperatures was calculated. The amount of water on the sample was calculated as the difference between the total weight loss and the amount of  $\text{NH}_3$  liberated. From this value, the amount of starting material on an anhydrous basis was calculated. The results are as follows:

TABLE N

$\text{NH}_4^+$ exchanged	20%	40%	60%	75%	85%	100%
Temperature $^\circ\text{C}$ .	% $\text{NH}_3$ Recovered					
100—225	14	10	11	14	12	14
225—350	50	42	46	34	46	47
350—475	30	40	32	41	35	32
475—600	7	8	10	8	5	10

Heating to a temperature of at least  $350^\circ\text{C}$ . is required to decompose a majority of the ammonium cations. A temperature of  $475^\circ\text{C}$ . gives about 90 per cent decomposition while  $600^\circ\text{C}$ . effects substantially complete decomposition of the ammonia.

Kjeldahl analysis of a sample of 75%  $\text{NH}_4^+$  exchanged material heated in dry air at  $550^\circ\text{C}$ . showed that 0.07 wt-%  $\text{N}_2$  remained in the material. Reheating this material under vacuum caused the removal of an amount of  $\text{NH}_3$  corresponding to this amount of  $\text{N}_2$ . A sample that had been heated to  $350^\circ\text{C}$ . to decompose 50—60% of the  $\text{NH}_4^+$  and then rehydrated was again reheated under vacuum. During the second heating, less than 10% additional  $\text{NH}_3$  was removed at

a temperature of  $350^\circ\text{C}$ . This showed that the thermal decationization is primarily dependent upon the temperature to which the sample is heated.

#### EXAMPLE IX

##### Decationization of $\text{NH}_4$ Exchanged Type Y Zeolites in Various Atmospheres

The effect of the atmosphere in which decomposition of the  $\text{NH}_4^+$  ion is effected was investigated. The same system as described in Example VIII was employed except a flow of the desired gas was passed through a sample heated to  $550^\circ\text{C}$ . The  $\text{NH}_4(75)\text{Y}$  powder samples were pelletized to prevent carry-off of the zeolite by the gas stream. The gases were dried prior to use.

The following data were obtained:

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TABLE O

Run	Atmosphere	Milliequivalent of $\text{NH}_3$ Liberated per gram Anhydrous Starting Material	Retention of Crystalline Structure
A	vacuum	3.26	almost complete
B	dry air—atm. press.	2.81	" "
C	dry air—atm. press.	2.74	" "
D	dry $\text{N}_2$ —atm. press.	3.26	" "
E	dry $\text{H}_2$ —atm. press.	3.29	" "

In the results shown above, the liberation of 3.26 to 3.29 milliequivalents of  $\text{NH}_3$  is indicative of substantially complete ammonia removal as checked by analysis of the product from the vacuum treatment which contained  $0.06 \pm 0.003\%$  of residual  $\text{N}_2$ . The lower value of the ammonia trapped during the air treatment results from partial oxidation of the ammonia.

## EXAMPLE X

## Adsorption Properties

The utility of the decationized Type Y molecular sieve zeolite was illustrated by its molecular sieving adsorption characteristics. The apparent pore size of the highly decationized material appeared to be somewhat smaller than that of the cationic sodium form. The pore size of the Type NaY is from 9–10Å. The pore size of the decationized Type Y is from 8–9Å. It was

found that the decationized Y molecular sieve will adsorb molecules commensurate with its pore size.

## EXAMPLE XI

## Hydrocracking Activity of Decationized Molecular Sieve Zeolite

In addition to other utilities, the decationized zeolitic molecular sieves of this invention are particularly useful in hydrocarbon cracking processes. A decationized Type Y zeolite was tested as a hydrocracking catalyst. It was found to possess hydrocracking activity superior to that of a commercial catalyst. The hydrocarbon feed used was n-heptane. Both materials were activated in  $\text{H}_2$  prior to testing in the standard procedure. The decationization of the  $\text{NH}_4^+$  Y illustrated an *in situ* activation of this material. The following results were obtained:

TABLE P

Material:	Decationized Na(20)Y		Commercial Catalyst	
Reaction Temp., °C.:	450	450	500	550
Products Formed (Mole—%)				
$\text{C}_1$ — $\text{C}_4$ fractions	75	4	8	42
% $\text{C}_1 + \text{C}_2$ in $\text{C}_1$ — $\text{C}_4$	3	0	10	12
% $\text{C}_3$ in $\text{C}_1$ — $\text{C}_4$	43	50	45	48
% $\text{C}_4$ in $\text{C}_1$ — $\text{C}_4$	54	50	45	40
% iso $\text{C}_4$ in $\text{C}_4$	72	45	49	55
% unreacted n — $\text{C}_7$	14	96	92	55

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These results revealed that the decationized Y was more active than the commercial cracking catalyst at a lower temperature. Furthermore, the product consisted of the more desirable propane and butane components. In the butane fraction, a large portion of the product was the desirable isobutane.

WHAT WE CLAIM IS:—

1. A decationized crystalline aluminosilicate zeolitic molecular sieve having a silicon dioxide to aluminum trioxide molar ratio greater than 3.0, a pore size of at least 5.6Å, capable of adsorbing benzene and in which at least 10% of the aluminium atoms of the zeolitic molecular sieve are not associated with cations.

2. A decationized metal aluminosilicate zeolitic molecular sieve as claimed in claim 1 having a silicon dioxide to aluminum trioxide molar ratio greater than 4.5, and in which at least 30% of the aluminium atoms of the zeolitic molecular sieve are not associated with cations.

3. A decationized zeolite as claimed in claim 2 in which at least 70% of the aluminium atoms of the zeolitic molecular sieve are not associated with cations.

4. A decationized zeolite Y, Zeolite L or faujasite as claimed in any of the preceding claims.

5. A process for the preparation of a decationized crystalline zeolitic aluminosilicate molecular sieve which comprises contacting a crystalline zeolitic molecular sieve having a silicon dioxide to aluminum trioxide ratio of greater than 3.0 and a pore size of at least 5.6Å, with a hydrogen or ammonium cation containing material thereby replacing at least 10% of the zeolitic cations with hydrogen or ammonium cations and thereafter removing the hydrogen or ammonium cations by heating the substituted zeolite at a tem-

perature of from 350° C. to 600° C.

6. A process as claimed in claim 5 in which the crystalline zeolitic molecular sieve metal cations prior to decationization are replaced with hydrogen cations by water leaching.

7. A process as claimed in claim 5, in which the crystalline zeolitic molecular sieve metal cations are replaced with hydrogen cations by contacting the zeolite with aqueous acids.

8. A process as claimed in claim 5, in which the crystalline zeolitic molecular sieve cations are replaced with ammonium cations by ion-exchanging the zeolitic metal cations with ammonium ions.

9. A process as claimed in any of claims 5 to 8 in which the zeolite is zeolite Y, Zeolite L or faujasite.

10. A process as claimed in any of claims 5 to 9 in which the ion-exchanged zeolite is heated at a temperature from 475° C. to 600° C.

11. A process as claimed in any of claims 5 to 10 in which the metal of the metal aluminosilicate is sodium, calcium, or silver.

12. A decationized zeolitic molecular sieve according to claim 1 substantially as described in any one of Examples 5, 8 or 9.

13. Process of preparing a decationized zeolitic molecular sieve according to claim 5 substantially as described in any one of the Examples 5, 8 or 9.

14. Process of cracking hydrocarbons wherein a hydrocarbon is heated in the presence of a decationized zeolitic molecular sieve as claimed in any of claims 1 to 4.

15. Process of hydrocracking hydrocarbons wherein a hydrocarbon is heated in the presence of a decationized zeolitic molecular sieve as claimed in any of claims 1 to 4.

W. P. THOMPSON & CO.,  
12, Church Street, Liverpool, 1.  
Chartered Patent Agents.

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